

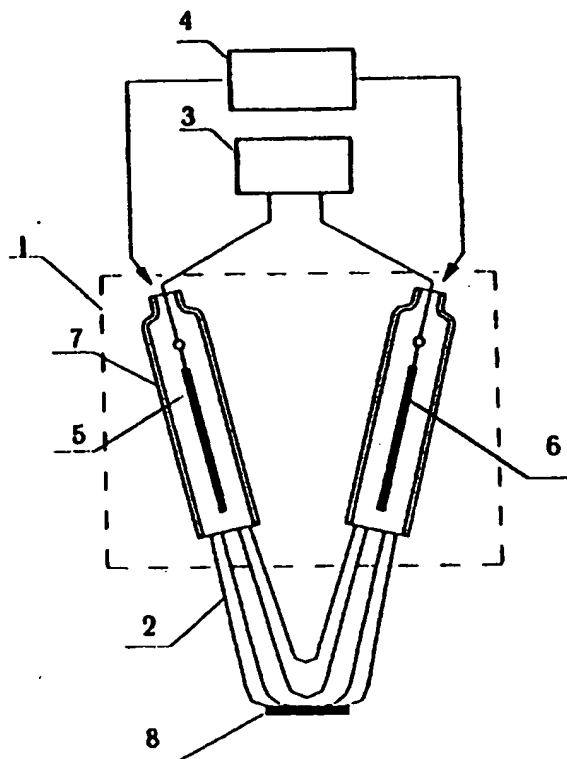
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(21) International Application Number: PCT/EP96/05653 (22) International Filing Date: 12 December 1996 (12.12.96) (30) Priority Data: 95120972 15 December 1995 (15.12.95) RU (71) Applicant (for all designated States except US): OPA (OVERSEAS PUBLISHERS ASSOCIATION) AMSTERDAM B.V. [NL/NL]; 1st floor, Amsteldijk 166, NL-1079 LH Amsterdam (NL). (72) Inventors; and (75) Inventors/Applicants (for US only): VAVILIN, Vladimir, M. [RU/RU]; K-498, 440/174, Moscow 103498 (RU). ERYOMKIN, Alexander, A. [RU/RU]; Rodionova St. 4/91, Khimky, Moscow Region 141499 (RU). (74) Agent: ORCHARD, Oliver, John; John Orchard & Co., Staple Inn Buildings North, High Holborn, London WC1V 7PZ (GB).		(81) Designated States: JP, KR, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>

(54) Title: METHOD AND APPARATUS FOR TREATMENT OF SURFACES**(57) Abstract**

A method and apparatus for use in treating the surface of a body, for example for sterilization, which includes supplying gas or gases to a discharge region in which an actuating plasma medium is formed as a result of applying a variable voltage to electrodes which partly define the discharge region.



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**METHOD AND APPARATUS FOR TREATMENT OF
SURFACES**

The present invention relates to a method and apparatus for use in the treatment of bodies and materials, and it has particular, though not exclusive, application in the disinfection and sterilization of
5 items used in the food industry and in medicine.

The specification of European Patent Application No. 90302410.7 describes a previously proposed method and apparatus for sterilization and disinfection.

This previously proposed method provides a high
10 quality of disinfection and sterilization combined with a relatively short processing time, but it requires expensive vacuum equipment. Moreover, because of the need to clean the working area regularly and to restore the vacuum additional time and energy are required.

15 A method for the sterilization and disinfection of medical equipment on the basis of a surface treatment using nitrogen and/or argon plasma jet has been previously proposed in the specification of Russian Federation Patent No. 2000811. The jet is produced by
20 supplying plasma-forming gases to a discharge gap, which is formed by at least two electrodes, with the subsequent excitation of the electric discharge and the processing of the target surface by means of the plasma jet.

In the specification of International Patent
25 Application No. PCT/EP92/01 131, there is described an

apparatus for the treatment of a solid body that includes an atmospheric pressure plasma generator, a plasma-forming gas supply system, a power supply, and a support for a body to be treated.

5 In the method and apparatus described in the specification of the international patent application, the gas is fed in such a way as to form and maintain a streamer plasma jet, which results in a comparatively high energy consumption. The plasma channel is elongated
10 and the energy consumption reaches 5-10 kW, the plasma-forming gas consumption being increased to 5 l/min. or more. The applications of this method and apparatus are seriously restricted. Because of the high temperatures involved, the method is not suitable for application to a
15 large number of materials, for example, to polymers, which are widely used in the food industry and in medicine.

 Features of arrangements to be described below, by way of example, in illustration of the present invention
20 are that the energy consumed by the process of surface sterilization is reduced and that the temperature of the treatment is reduced, while a high quality of treatment is obtained. Moreover, the method enables regions, such as the inner surfaces of containers, pipes, flasks,
25 catheters, which are difficult to reach to be treated.

 A method to be described below, in illustration of the present invention, is an improvement in the method proposed in the above-mentioned Russian Federation

patent. It is proposed to supply plasma-forming gas or gases under atmospheric pressure to a discharge gap formed by at least two electrodes, to exit a discharge, and to introduce a surface to be treated into a processing zone. It is proposed that the surface of a body should be treated by an actuating plasma medium, which takes the shape of the body during direct contact with it. The initiation of an electric discharge is obtained by applying a voltage with a changing value sufficient to form an actuating plasma medium. Plasma-forming gases may be inert gases and/or nitrogen and/or oxygen and/or their mixtures, as well as their mixtures with other gases. It is also proposed that the plasma medium may be modified by altering the ratio of plasma-forming gases and/or electric discharge power and that the surface may be treated by moving it and the actuating plasma medium relative to one another. The method can be applied to materials, tools, containers and other objects used in food, medical, and the pharmaceutical industries.

20 A plasma-forming gas or mixture is fed to and fills the electrode gap, and a peak voltage which exceeds the breakdown voltage of the electrode system when filled with the gas, is applied to the electrodes. It is of special importance to provide direct contact between the electrode gap and the gas source because, should gas be absent, the gap is likely to become filled with air, and the initiation of a plasma discharge in such an air gap will require higher voltage and a greater expenditure of

energy in order to maintain the discharge. Thus, the supply of a plasma-forming gas to the electrode gap stimulates the formation of the actuating plasma medium upon the application of a given voltage applied to the electrodes. Plasma can also be generated by a voltage with a changing value if a plasma forming gas fills a part of the discharge gap and the electric field is strong enough to break down the gas layer. The air layer of the gap serves as the dielectric of the capacitor formed by the electrode and the plasma-forming gas layer.

In order to achieve the best formation of a plasma medium, plasma-forming gas should be supplied either (a) through a tube or a nozzle whose output end is placed directly in the electrode gap, or (b) through a tube or several tubes whose output ends are some way from the gap, but so arranged that the axis of symmetry of the gas flow produced by each of the tubes, or the axis of symmetry of the resultant joint gas flows, passes to the electrode gap.

In a particular embodiment to be described below, in illustration of the invention, a body to be treated is placed so that the surface of the body, or a part of it, is in the plasma medium area and is processed by the plasma-induced diffusion flow of active particles toward the surface of the body. Upon reaching the surface, the particles sterilize the micro-organisms on it. The particle flux density and, hence, the efficiency of the killing effect of the plasma particles depend upon their

concentration in the plasma medium. In other words, the efficiency is higher the less equilibrium there is in the plasma. The plasma medium may be made to be substantially out of equilibrium by specially selecting the variation with time in the pattern of the voltage applied to the electrodes. Pulse or sinusoidal RF voltage patterns are the most effective.

The method can be implemented with an apparatus including an atmospheric pressure plasma generator, a gas source, a power supply, and a support of a body to be treated. The plasma generator, operating as an actuating plasma medium generator, includes, at least two electrodes connected with the power supply, the electrode gap being in direct contact with the gas supplying system, and the support for a body to be treated being so arranged that the body is placed in the discharge gap.

To minimize the size of the apparatus and to reduce its power consumption, one of the electrodes may constitute the support for the body. In this case, the body to be treated is placed on a flat electrode in the discharge gap.

Also, in order to reduce the size of the device, to minimize gas consumption, and to increase the concentration of active particles in the actuating plasma medium as a result of reducing its volume, the electrodes may be made in the form of dielectric tubes connected with the gas supplying system.

The spatial parameters of the actuating plasma

medium are largely determined by the mode of the gas flow in the electrode gap. In order for the gas to fill the gap homogeneously, irrespective of the gas supply method, a dielectric container may be placed between the electrodes, and the gas is supplied to this container. The support with a body to be treated is also placed in the container. For this setup, the spatial distribution of the actuating plasma medium in the container is determined by its interaction with the container walls. Thus, the shape of the actuating plasma medium can be controlled by selecting the shape of the container.

In many cases, the body to be treated needs no special support and can be placed on the inner wall of the container. Then the shape of the wall is chosen so as to achieve the optimum process conditions.

To increase the homogeneity of the electric discharge distribution in the container (and, hence, the homogeneity of the plasma medium distribution), it is possible to make at least one of the electrodes elongated and so that it embraces the container.

To reduce the amount of energy spent on the generation and maintenance of the actuating plasma medium, at least one of the electrodes may be placed in the container. Thus, it is possible to reduce the gap between the electrodes and to lower the amount of energy required for initiating the plasma discharge.

One important application of the method and apparatus to be described below in illustration of the

invention is the treatment of the inner surfaces of empty bodies, such as bottles, flasks, and other vessels used for fluids and free-flowing bulk materials in food, medical, and other industries.

5 The working principle of such a device is similar to that of a device employing a container, with the exception that the treated hollow object serves as the container itself.

10 If the surface to be processed is larger than the size of the actuating plasma medium, the surface and the plasma medium may be moved relative to each other so that the plasma scans the surface. Such devices are useful in the processing of packaging material or the inner walls of pipes. Furthermore the arrangement of the system may
15 vary depending on the purpose of the device. The system may include, for example, temperature gauges, sensors of the composition and shape of the plasma medium, and of the temperature and shape of the body to be treated.

20 An important characteristic of arrangements to be described below, in illustration of this invention is the way in which the state and shape of the plasma is organised as a physical factor impacting upon the surface of the body to be treated. In earlier proposals, the terms "plasma jet" and "plasma jet generator" were used,
25 whilst in the arrangements to be described below, the terms "actuating plasma medium" and "actuating plasma medium generator" are particularly mentioned. These terms are not equivalent to the terms used previously,

because their sense is important in achieving the best effect of the plasma on the surface.

Unlike a plasma jet, an actuating plasma medium excludes the dynamic component of plasma propagation, distribution and impact on the material; it also has a smaller volume, i.e. there is a smaller plasma channel length. Besides, a "Jet" and a "Medium" differ in the manner in which they treat the surface: a plasma jet can damage the structure of some materials and saturate them with oxygen, thus severely reducing the stability of the resultant properties of the material. Moreover, a jet has a limitation upon the scale of its effect on the surface, the so-called "impact or effect zone," as the jet contacts the surface, the area over which the effect occurs is limited by the cross-sectional area of the jet. For the actuating plasma medium, this area is only dependent on the size and shape of the surface, which determine the size and shape of the actuating plasma medium.

Embodiments illustrative of the invention will now be described by way of example only with reference to the accompanying drawings, in which:

Fig. 1 is a diagrammatic view of an apparatus for use in the sterilization of the outer surfaces of a body with electrodes placed in tubes,

Fig. 2 is a diagrammatic illustration of an apparatus for use in the sterilization of the outer surfaces of a body in which one of the electrodes is flat

and is used as a support for a body to be treated,

Fig. 3 is a diagrammatic view of an apparatus for use in the sterilization of the contents of a dielectric container placed between electrodes,

5 Fig. 4 is a diagrammatic view of an apparatus for use in the sterilization of the contents of a dielectric container with one electrode in the container,

Fig. 5 is a diagrammatic view of an apparatus for use in the sterilization of the inner surfaces of flasks
10 or other such vessels, and

Fig. 6 shows diagrammatic longitudinal and cross-sectional views of an apparatus for use in the sterilization of the inner surfaces of dielectric tubes.

In the various Figures, corresponding elements will
15 be designated by the same reference numerals.

Referring to Fig. 1, there is shown a view which enables the working principle of an apparatus for use in the sterilization and disinfection of a body to be explained.

20 In this embodiment a simple device setup is shown. It includes an atmospheric pressure actuating plasma medium generator 1 which produces an actuating plasma medium indicated at 2, an AC power supply 3, and an argon gas supply system 4. The generator 1 has electrodes 5
25 and 6 in the form of tungsten rods quartz tubes 7. The tubes 7 are connected with the argon source 4. The electrodes 5 and 6 are arranged at an angle of 65° with each other, the minimum distance between them being 8 mm.

It will be understood that the angle and the distance may be varied according to the parameters of the body to be treated and the apparatus. The angle may be varied from 0° upwards.

5 In operation, argon is fed from the source 4 through the quartz tubes 7 to a region between the ends of the electrodes and the surface of a body 8 to be treated at a rate of 0.2 l/min. The power source 3 excites an electric discharge between the electrodes 5 and 6 at
10 atmospheric pressure. The frequency of the voltage is 110 kHz, and its amplitude is 4 kV. Thus, an actuating plasma medium 2 is formed. The desired heating flux density at the surface of the body 8 to be treated is maintained by varying the argon consumption and it may be
15 monitored by a pyroelectric or bolometric gauge (not shown in Fig. 1) that is placed in the plasma medium during its stabilization and then removed. During the formation of the plasma medium 2, the body 8 with the surface to be treated is placed at a distance of 8 mm
20 from the output ends of the tubes 7. The process control is such that no part of the surface to be treated is affected by the plasma medium for longer than 0.5 s.

 It should be noted that the thermal effect of the actuating plasma medium is not the only mechanism that
25 affects the desired result. The magnitude of the heat flux is one of the most easily and rapidly measured parameters of the actuating plasma medium. Knowing the value of heat flux, enables quite adequate estimates of

other plasma medium parameters to be made.

Referring to Figure 2 there is shown an apparatus in which one of the electrodes 6 is flat and serves as the support for a body 8 to be treated. This electrode 6 is
5 in the form of a conveyor belt, which carries the treated body 8. The conveyor is driven by a drive mechanism 9, thereby providing mutual movement between the actuating plasma medium generator and the surface of the body 8 to be treated. The second electrode 5 is in the form of a
10 metal tube with an outer diameter of 10 mm. and an inner diameter of 2 mm, and it is connected with the gas supply system 4. The electrodes 5 and 6 are connected to the power supply 3. The distance between the electrodes 5 and 6 is 5 mm.

15 A pyroelectric contactless temperature gauge 10 is placed in the immediate vicinity of the electrode gap and is connected with a signal processing unit 11. The gauge 10 measures the temperature of the treated surface immediately after plasma medium has been brought into
20 effect.

Figure 3 shows an apparatus for generating an actuating plasma medium in a container placed between the electrodes 5 and 6. The device shown in Fig. 3 includes a container 12, in the form of a quartz vessel, with a
25 diameter of 50 mm. and a depth of 70 mm, a cover 13 which has a gas supply channel 14 at its centre and which is spaced by 2 mm from the container walls, the gas source 4, which feeds gas through the channel 14 to the

container 12, and two electrodes 5 and 6 connected to the power supply 3. The electrodes 5, which is flat, is placed on the outer side of the cover 13 and the electrode 6 is placed on the outer side of the container 12 which it embraces in the form of a ring. The object 8 to be treated is placed on the bottom of the container 12.

The apparatus operates in an analogous way to the previously described arrangements. Gas is fed from the source 4 through the channel 14 of the cover 13 into the container 12, and then the power source 3 is switched on. Gas fills the entire volume of the vessel, flowing around the body 8 to be treated, takes its shape, and then leaves the container through a gap between the inner wall of the container 12 and the edge of the cover 13.

A plasma discharge is initiated in the vessel between the electrodes 5 and 6 at a frequency of 180 kHz and in a field of about 5×10^4 V/m. The cover 13 is initially placed at a distance of 10 mm from the bottom of the container 12. The gas consumption is 0.8 l/min.

After the discharge has been initiated, the cover 13 is raised to 50 mm from the bottom of the container 12, and the gas supply is gradually increased to 1.3 l/min. The heat flux density of the treated surfaces is maintained at a level of 7.5×10^4 W/m². The power supply 3 is switched on for 3 to 5 seconds.

Figure 4 shows an apparatus that is similar to that shown in Fig. 3, but which differs in the shapes and the

positions of the electrodes 5 and 6. The electrode 5 is placed on the inner side of the cover 13 and a TV camera 15 is provided which enables the optical properties of the plasma medium in the container 12 to be monitored.

5 The camera 15 is connected to a signal processing unit 16.

In Figure 5 there is shown an apparatus for treating the inner surfaces of hollow bodies. An object to be treated is placed in a glass medical flask 8. Electrodes 10 5 and 6 are arranged coaxially and are fixed on to an insulating plate 17. The electrode 5 is placed centrally in the flask 8 and is in the form of a tube connected to a gas source 4. The operating sequence of the apparatus is similar to that of the apparatus described with 15 reference to Fig. 4. For a 10 ml flask, the electric field intensity was 450 V/mm, the argon volume flux was 1.6 l/min., and the treatment time was 15 seconds.

Figure 6 shows an apparatus for treating the inner surfaces of elongated dielectric tubes. The apparatus is 20 an actuating plasma medium generator which includes a power supply 3, and a gas source 4. The generator has one pair of electrodes 5 and 6 connected to a power source 3. The electrodes 5 and 6 are in the form of rectangular copper plates bent around the cylindrical 25 surface of the tube 8 to be treated. A flange 18 connects the electrodes 5 and 6 with tangential 19 and axial 9 drives. A tube 8 to be treated has an outer diameter of 12 mm and an inner diameter of 10 mm. The

angular width of the contact areas of each of the electrodes 5 and 6 with the tube 8 extends over an arc of 65 degrees, the lengths of the electrodes being 25 mm.

The operating sequence of the device is as follows.

5 In operation, argon was fed to the tube 8 from the source 4 at a rate of 0.8 l/min. A voltage of 7500 V at a frequency of 110 kHz was applied to the electrodes 5 and 6. The output power of the power supply was 325 W, and the electric field intensity in the tube 8 was 5×10^2
10 V/mm.

Under the above working conditions, the heat flux density in the tube 8 was 3.5×10^4 W/m².

The electrodes 5 and 6 are moved by the drives 19 and 9 around the tube with a speed of 0.5 rps and along
15 the axial length of the tube at a speed of 0.12 m/s.

Under these conditions, a sterilizing plasma medium is generated in the tube 8. Because of the rotational and axial movements of the electrodes 5 and 6, the actuating plasma medium fills the entire volume of the
20 tube 8 and contacts the whole of its inner surface.

Having thus described particular arrangements, by way of example, in illustration of the invention, it will be apparent to those skilled in the art that various modifications and other embodiments can be made within
25 the scope of the appended claims.

For example, using more than one pair of electrodes in the actuating plasma medium generator, it is possible to increase the concentration of active particles in the

plasma medium and, hence to increase the efficiency of the methods described.

The methods described have been tested in the food industry for the sterilization of polyethylene films used for the packaging of food products. The specimens were prepared and tested at the Research Institute for Practical Toxicology and Disinfection of the State Epidemiological Committee of the Russian Federation. The results showed that after treatment there was no germination of test microbiological cultures which had been planted on the films before plasma medium treatment took place.

Medical tests of the methods were also performed at the Departments of Introductory Orthopaedic Stomatology and Microbiology, Immunology and Virology of the Semashko Dentistry Institute, Moscow.

Test objects in the form of 48 tooth moulds infected with samples of typical mouth microflora were treated. It was shown that, after treatment, the moulds could be used for the preparation of dentures. The tests showed that the methods described above in illustration of the present invention were highly efficient in treating the infections.

The method was also tested for one of the most common microbes of mouth microflora, *Candida albicans*. 10^9 ml^{-1} solutions of these test cultures were deposited

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on plates of tooth mould material. After the plates had been treated using the methods described above no micro-organisms grew on any of the samples.

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CLAIMS

1. A method for use in treating a surface of a body including the steps of supplying a plasma-forming
5 gas or gases at atmospheric pressure to a discharge region associated with two electrodes, stimulating an electric discharge in the region, and introducing the surface to be treated into the region, in which the electrical discharge is stimulated in the region by
10 applying a voltage having a changing value between the electrodes, the voltage being sufficient to cause the formation of an actuating plasma medium, which is in direct contact with the surface to be treated and which follows the shape of the surface to be treated.
- 15
2. A method as claimed in claim 1 in which plasma-forming gas or gases are inert gases and/or nitrogen and/or oxygen and/or mixtures thereof.
- 20
3. A method as claimed in either claim 1 or claim 2 in which the actuating plasma medium is controlled by varying the ratio between the supply of plasma-forming gases and/or the power applied to the electric discharge.
- 25
4. A method as claimed in any one of the preceding claims in which the actuating plasma medium and the surface of a body to be treated are moved relative to one another.

5. A method as claimed in any one of the preceding claims in which the surface to be treated is the surface of a medical instrument.

5 6. A method as claimed in any one of the preceding claims in which the surface to be treated is the surface of a container or vessel, or other object to be used in medicine, or in the pharmaceutical or the food industry.

10 7. A method as claimed in any one of the preceding claims in which the surface to be treated is the inner surface of a hollow body.

 8. A method as claimed in any one of the
15 proceeding claims in which the parameters of a surface being treated and/or of the actuating plasma medium are monitored during the operation of the method.

 9. A method as claimed in any one of the preceding
20 claims for use in the sterilization of the inner surface of a hollow body in which the electrodes are arranged on the outside of the hollow body.

 10. An apparatus for use in treating a surface of a
25 body including a generator for generating a plasma at atmospheric pressure, the generator having two electrodes, a power supply connected to the electrodes, a plasma-forming gas supply system and a support for a body

to be treated, the plasma-forming gas supply system supplying a gas or gases to a discharge region associated with the electrodes, in which the support is arranged to allow the surface of the body to be treated to be placed
5 in the discharge region the electrodes being so designed and arranged in relation to the surface of the body to be treated that, upon the application of a voltage having a varying value to the electrodes the plasma generator provides an actuating plasma medium that in operation
10 takes the shape of and is in contact with the surface of a body to be treated.

11. An apparatus as claimed in claim 10 in which the electrodes are in dielectric tubes connected with the
15 gas supply system.

12. An apparatus as claimed in claim 10 in which one of the electrodes is flat.

20 13. An apparatus as claimed in claim 10 which includes a dielectric container connected with the gas supply system, the support for a body to be treated being within the container.

25 14. An apparatus as claimed in claim 13 in which at least one of the electrodes is elongated and embraces the container wall.

15. An apparatus as claimed in claim 13 in which one of the electrodes is within the container.

16. An apparatus as claimed in claim 10 in which
5 the inner surface of a hollow body to be treated is connected with the gas supply system, and one of the electrodes is placed within the region defined by the inner surface.

10 17. An apparatus as claimed in any one of claims 6 - 16 in which the generated actuating plasma medium and the support for the surface of a body to be treated are relatively movable.

15 18. An apparatus as claimed in any one of claims 6 - 17 which includes a system for monitoring parameters of the treated surface and of the actuating plasma medium.

19. An apparatus as claimed in claim 10 for use in
20 the sterilization of the inner surface of a hollow body in which the electrodes are arranged on the outside of the hollow body.

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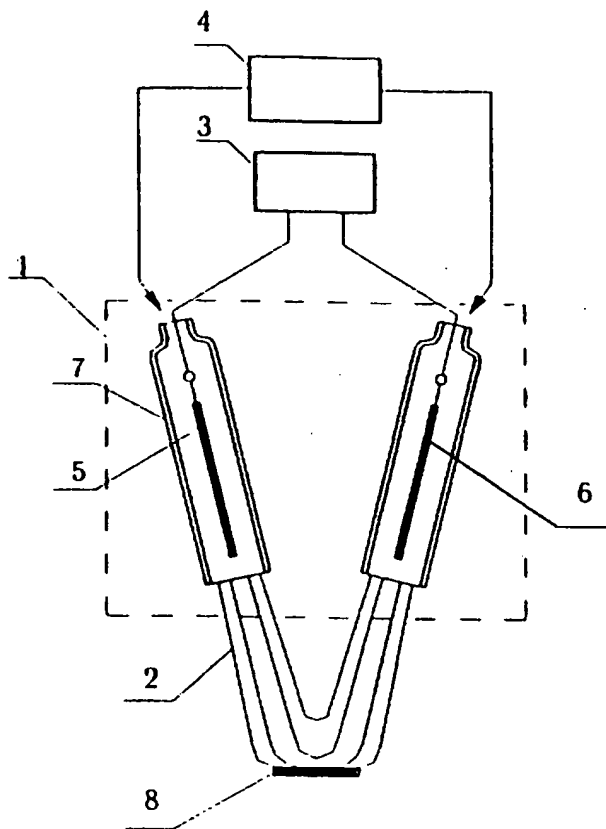


Fig.1

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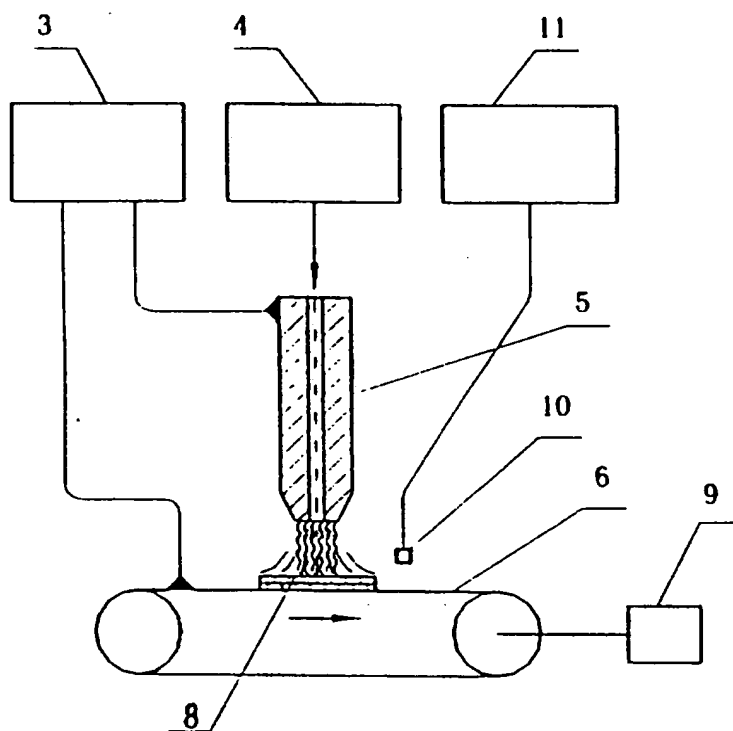


Fig.2

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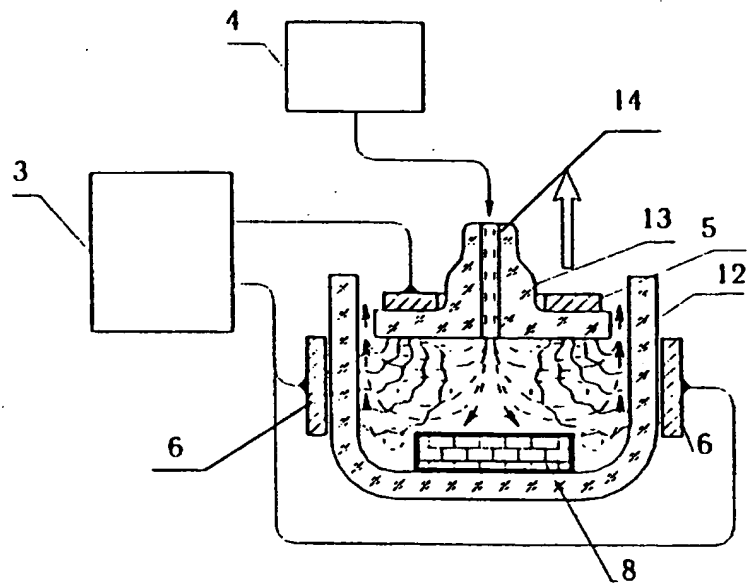


Fig.3

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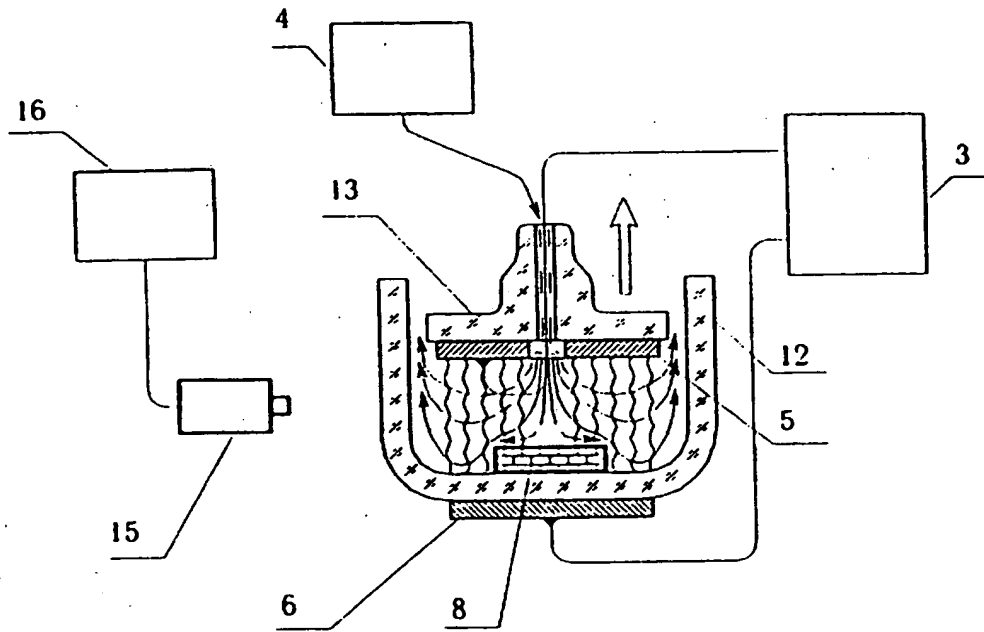


Fig.4

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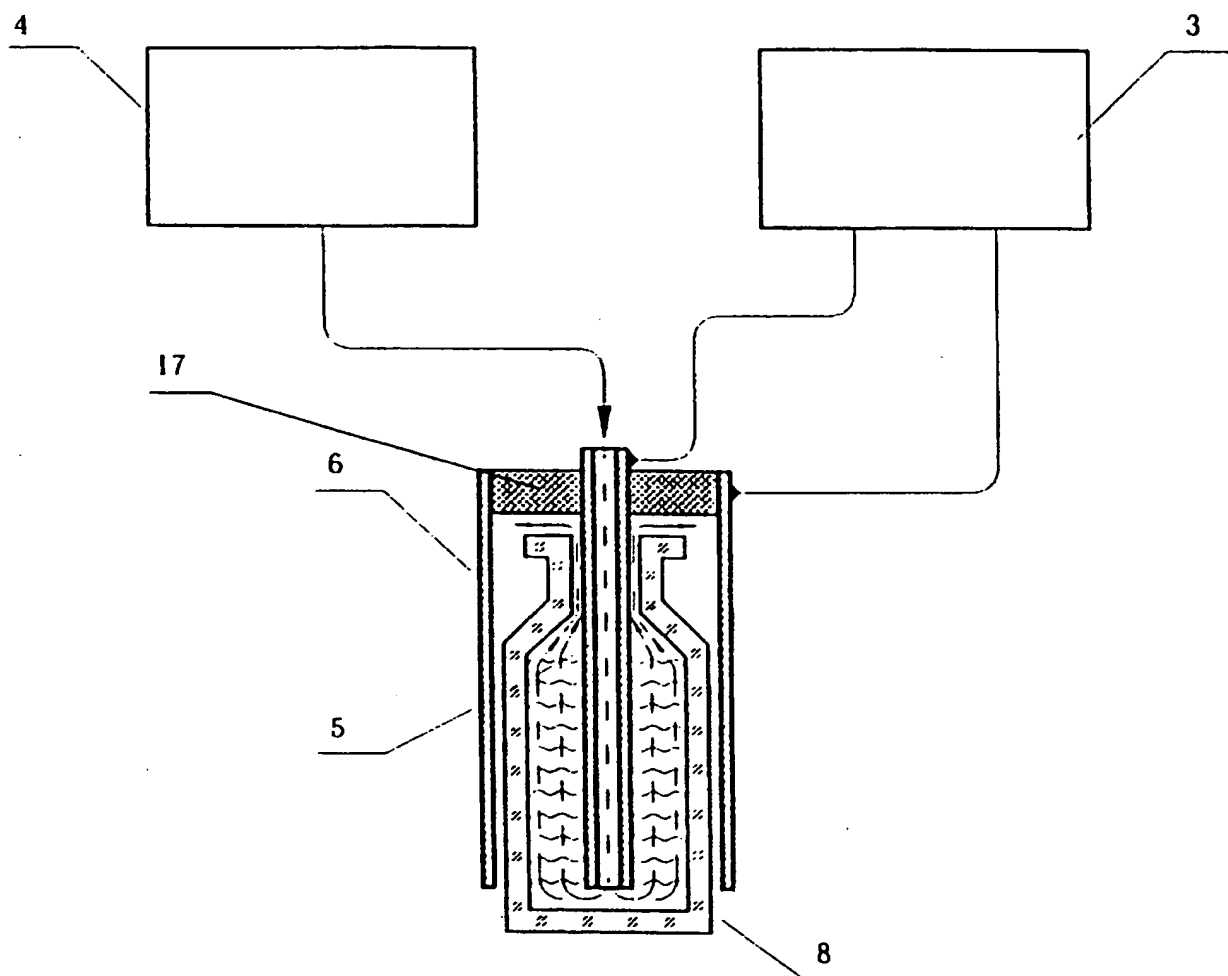


Fig.5

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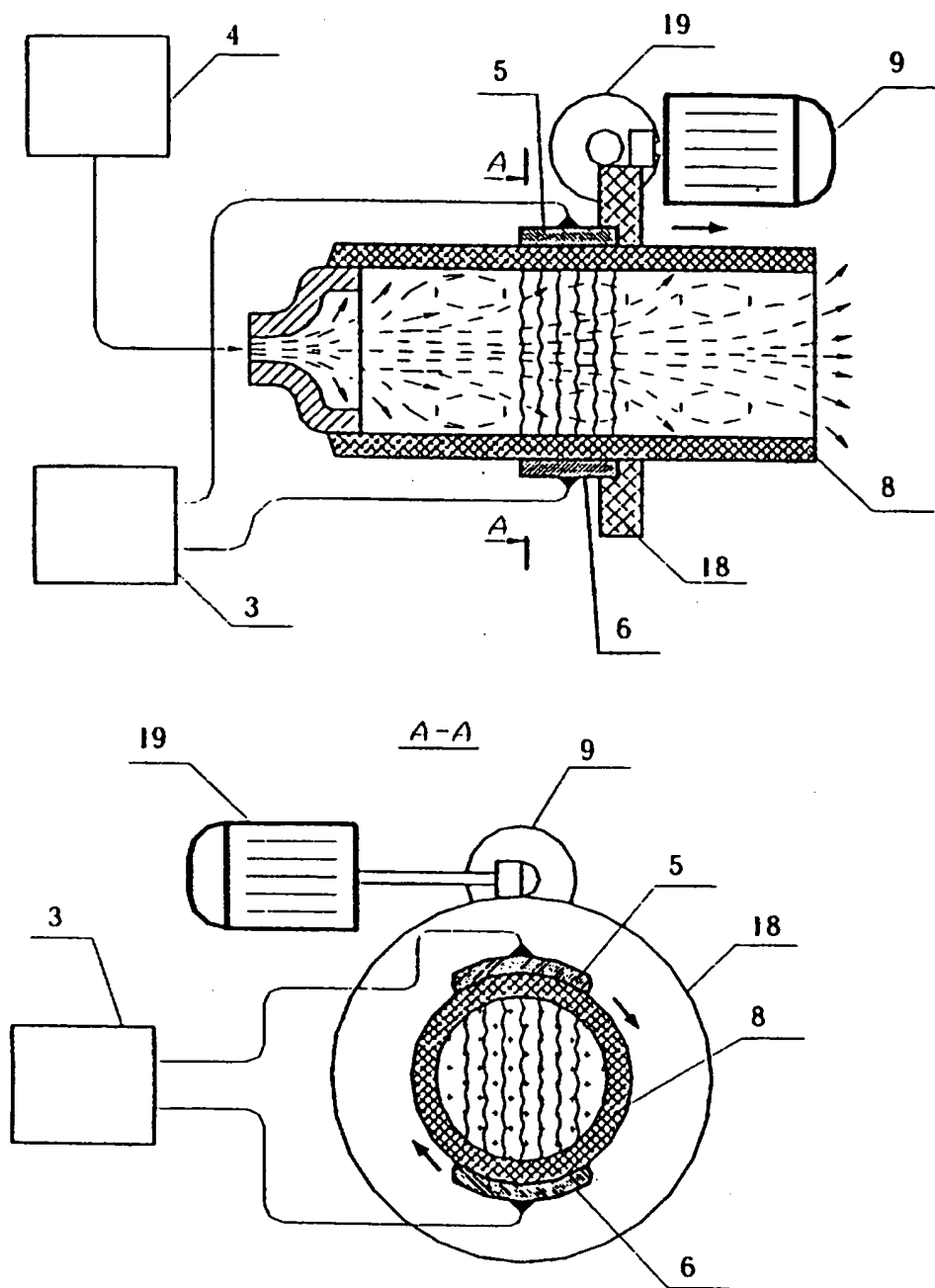


Fig.6

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 96/05653

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 A61L2/14 A23L3/26

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 A61L A23L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 3 383 163 A (MENASHI WILSON P) 14 May 1968 see claims; figures ---	1-19
A	FR 2 169 814 A (BOEING CO) 14 September 1973 see claims ---	1-19
A	EP 0 387 022 A (ABTOX INC) 12 September 1990 cited in the application see claims ---	1-19
A	WO 93 07908 A (OPA OVERSEAS PUBLISHERS ASS) 29 April 1993 see the whole document & RU 2 000 811 A cited in the application -----	1-19



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Date of the actual completion of the international search

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Information on patent family members

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 3383163 A	14-05-68	NONE	
FR 2169814 A	14-09-73	US 3851436 A	03-12-74
		CA 1004823 A	08-02-77
		CA 990925 A	15-06-76
		DE 2260854 A	20-06-73
		GB 1416723 A	03-12-75
		JP 48065796 A	10-09-73
EP 0387022 A	12-09-90	AT 113847 T	15-11-94
		DE 69013947 D	15-12-94
		DE 69013947 T	18-05-95
		ES 2066969 T	16-03-95
		JP 2279160 A	15-11-90
		US 5413759 A	09-05-95
		US 5472664 A	05-12-95
		US 5593649 A	14-01-97
		US 5115166 A	19-05-92
		US 5186893 A	16-02-93
		US 5178829 A	12-01-93
		US 5413760 A	09-05-95
		US 5288460 A	22-02-94
WO 9307908 A	29-04-93	RU 2000811 C	15-10-93
		EP 0611307 A	24-08-94